

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C08J 9/14, 9/12 // C08L 25:04</b>		A1	(11) International Publication Number: <b>WO 96/34038</b> (43) International Publication Date: 31 October 1996 (31.10.96)
(21) International Application Number: PCT/US96/04009 (22) International Filing Date: 21 March 1996 (21.03.96)  (30) Priority Data: 08/430,783 27 April 1995 (27.04.95) US 08/595,696 2 February 1996 (02.02.96) US  (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).  (72) Inventors: SHMIDT, Creston, D.; 4161 Briarcliff Road North- east, Nashport, OH 43830 (US). IMEOKPARIA, Daniel, D.; 9063 Indian Mound Road, Pickerington, OH 43147 (US). SUH, Kyung, W.; 1533 Welsh Hills Road, Granville, OH 43023 (US). MALONE, Bruce, A.; 3130 Granview Drive, Granville, OH 43023 (US). FRANKLIN, Ken; 925 Hartney Drive, Gahanna, OH 43230 (US).  (74) Agent: DEAN, J., Robert, Jr.; The Dow Chemical Company, Patent Dept., P.O. Box 515, Granville, OH 43023-0515 (US).		(81) Designated States: CA, FI, JP, KR, MX, NO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report.	
(54) Title: EXTRUDED, OPEN-CELL MICROCELLULAR FOAMS, AND THEIR PREPARATION PROCESS			
(57) Abstract  Disclosed is an extruded, open-cell microcellular alkenyl aromatic polymer foam useful in insulating applications. The foam has an open cell content of 70 percent or more. The foam has an average cell size of 70 micrometers or less. The foam is particularly useful in evacuated or vacuum insulation panels. Further disclosed is a process for making the open-cell foam.			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## Extruded, open-cell microcellular foams, and their preparation process.

5 This invention relates to an extruded, open-cell microcellular alkenyl aromatic polymer foam and a process for making.

To significantly improve the performance of insulating systems, vacuum panel technology is currently being evaluated by industry. The absence of air or gas in the panels affords the possibility of substantial enhancement of insulating performance.

10 To further significantly improve the performance of insulating systems, microcellular foams (for example, 70 micrometers or less) are being evaluated by industry. The small cell size affords the possibility of substantial enhancement of insulating performance in many instances.

Extruded, closed-cell alkenyl aromatic polymer foams of medium cell size (for example, 0.2 to 1.0 millimeter (mm)) have been employed in insulating systems for decades. 15 They offer good insulating performance and excellent mechanical strength. However, the closed-cell structure makes them unsuitable for use in vacuum systems. Closed-cell foams cannot be evacuated of entrapped gas easily or without collapsing them.

A means to address the problem of inability to evacuate would be to employ an alkenyl aromatic polymer foam with very high open cell content. However, the only known 20 microcellular, open-cell alkenyl aromatic polymer foams are those prepared by phase separation or with supercritical fluids as seen in U.S. Patent Nos. 4,673,695; 4,473,665; 5,158,986; and 5,334,356. These foams are expensive to produce and have limited mechanical strength.

25 It would be desirable to have a strong, economical, microcellular, open-cell alkenyl aromatic polymer foam to employ in vacuum insulation systems. It would further be desirable to have such foams in a cell size range of 70 micrometers or less.

According to the present invention, there is an extruded, open-cell microcellular alkenyl aromatic polymer foam. The foam comprises an alkenyl aromatic polymer material comprising greater than 50 percent by weight of alkenyl aromatic monomeric units. The foam 30 has an open cell content of 70 percent or more. The foam has an average cell size of 70 micrometers or less. The foam is useful in insulating applications and particularly useful in vacuum insulation panels.

Further according to the present invention, there is a process for making an extruded, open-cell microcellular alkenyl aromatic polymer foam having an open cell content 35 of 70 percent or more and an average cell size of 70 micrometers or less. The process comprises:

- a) heating an alkenyl aromatic polymer material to form a melt polymer material;
- b) incorporating into the melt polymer material an amount of a nucleating agent additive;
- c) incorporating into the melt polymer material at an elevated pressure to form a foamable gel a

blowing agent of which 70 mole percent or more is selected from the group consisting of 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoroethane (HFC-134a), chlorodifluoromethane (HCFC-22), carbon dioxide (CO<sub>2</sub>), and difluoromethane (HFC-32), and mixtures of the foregoing based upon the total number of moles of blowing agent, the blowing agent being present at 0.06 to 0.17 gram-moles or less per kilogram of polymer material; d) cooling the foamable gel to a foaming temperature sufficient to form a foam having 70 percent or more open cell content; and e) extruding the foamable gel through a die into a region of lower pressure to form the foam.

Further according to the present invention, there is an evacuated insulation panel comprising the open-cell foam described above in a hermetically-sealed receptacle. The evacuated insulation panel provides excellent insulation performance.

Extruded alkenyl aromatic polymer foams of high open cell content (70 percent or more) and microcellular cell size (70 micrometers or less) are heretofore unknown in the art. Such extruded foams have been deemed difficult to produce because of insufficient degree of nucleation, foam collapse, poor skin quality, and excessive density.

The present process achieves sufficient nucleation and forms the present foam by employing each of the following: a nucleating agent additive; a blowing agent which has a relatively high intrinsic nucleation potential; an amount of a blowing agent small enough to allow formation of an open-cell structure; and a relatively high foaming temperature to allow formation of an open-cell structure.

It is desirable to achieve the necessary level of nucleation with minimum processing difficulties in the extrusion system and maintain desirable end product foam properties. Processing difficulties are typically minimized when as much as possible of the requisite nucleation potential is obtained from the blowing agent and the least possible from the nucleating agent additive while maintaining desirable end product foam properties. Nucleating agent additives, in excessive amounts, can substantially alter processing properties such as gel viscosity and die pressure and end product foam properties such as skin quality, compressive strength, cross-section, and density. Incorporation of the nucleating agent additive is nonetheless an essential component of the extrusion process because the necessary nucleation potential cannot be attained with the blowing agent alone.

The amount of a nucleating agent additive employed to prepare the present open-cell foam will vary according to the desired cell size, foaming temperature, composition of the blowing agent, and composition and activity of the nucleating agent additive itself. Cell size decreases and open cell content increases with increasing nucleating agent content. Useful nucleating agents additives include inorganic substances such as calcium carbonate, talc, clay, titanium oxide, silica, barium sulfate, calcium stearate, styrene/maleic anhydride copolymer, diatomaceous earth, and mixtures of citric acid and sodium bicarbonate. The amount of

nucleating agent employed may range from 0.01 to 5 parts by weight per hundred parts by weight of a polymer resin. The preferred range is from 0.1 to 3 parts by weight.

5 The blowing agent must be capable of imparting a high degree of nucleation in conjunction with the nucleating agent additive to ensure formation of a foam with the desired cell size and open cell content. Suitable blowing agents will have a relatively high intrinsic nucleation potential at temperatures and pressures in which alkenyl aromatic polymers, such as polystyrene, are typically extrusion-foamed. Suitable blowing agents affording a high degree of nucleation include 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a); 1,1,1,2-tetrafluoroethane (HFC-134a), chlorodifluoromethane (HCFC-22), carbon dioxide (CO<sub>2</sub>), and  
10 difluoromethane (HFC-32). Preferred blowing agents are HFC-152a, HFC-134a, and carbon dioxide. The above blowing agents will comprise 50 mole percent or more and preferably 70 percent or more of the total number of moles of blowing agent.

Blowing agents useful as co-blowing agents with the above agents include inorganic agents and organic blowing agents. Suitable inorganic blowing agents include  
15 water, argon, nitrogen, and helium. Organic blowing agents include aliphatic hydrocarbons having 1-9 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Aliphatic alcohols include methanol, ethanol, n-propanol, and isopropanol. Fully and  
20 partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, pentafluoroethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons include  
25 methyl chloride, methylene chloride, ethyl chloride (EtCl), 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11),  
30 dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane.

Another important feature of the invention is the amount of blowing agent incorporated into the polymer melt material to make a foam-forming polymer gel. The amount employed is from 0.06 to 0.17 gram-moles per kilogram of polymer, preferably from  
35 0.08 to 0.12 gram-moles per kilogram of polymer, and most preferably from 0.09-0.10 gram-moles per kilogram of polymer. The use of a relatively small amount of blowing agent allows formation of a foam with a high open cell content.

Another important feature of the present invention is foaming temperature. The foaming temperature must be high enough to prevent premature stabilization of the expanding foam cells until rupture of the foam cell walls is achieved. The foams of the present invention are susceptible to premature cooling because of their small cell size and high open cell content. The small cell size causes rapid initial expansion of the foam upon exiting the die resulting in the rapid cooling of the foam. The high open cell content creates an open physical structure for heat and blowing agent to escape resulting in additional rapid cooling. The present invention compensates for the rapid cooling of the foam by foaming at a temperature greater than that typically employed for foam with larger cell sizes and smaller open cell contents.

The foaming temperature must not however, be so high as to cause other processing or product problems. Because of the high open cell content of the foam, excessively high foaming temperatures can cause foam collapse due to rapid loss of blowing agent and reduced ability of cell struts to resist ambient pressure. Thus, the foaming temperature must be high enough to prevent premature cooling of the foam, yet low enough to prevent its collapse. Further, high foaming temperatures can reduce extrusion die pressures to unacceptably low levels and negatively impact skin quality. The most desirable foaming temperature will be the lowest foaming temperature at which the foam can be made and still maintain the open cell structure.

Desirable foaming temperatures will depend upon factors including the configuration of the extrusion system, nucleating agent additive composition and concentration, blowing agent composition and concentration, polymer material characteristics, and extrusion die design. Preferred foaming temperatures will vary from 118°C to 160°C. Most preferred foaming temperatures will vary from 125°C to 135°C.

The present foam is generally prepared by heating an alkenyl aromatic polymer material to form a plasticized or melt polymer material, incorporating therein a blowing agent to form a foamable gel, and extruding the gel through a die to form the foam product. Prior to mixing with the blowing agent, the polymer material is heated to a temperature at or above its glass transition temperature or melting point. The blowing agent may be incorporated or mixed into the melt polymer material by any means known in the art such as with an extruder, mixer, or blender. The blowing agent is mixed with the melt polymer material at an elevated pressure sufficient to prevent substantial expansion of the melt polymer material and to generally disperse the blowing agent homogeneously therein. The nucleating agent additive may be blended in the polymer melt or dry blended with the polymer material prior to plasticizing or melting. The foamable gel is typically cooled to a lower temperature to optimize or attain desired physical characteristics of the foam. The gel may be cooled in the extruder or other mixing device or in separate coolers. The gel is then extruded or conveyed through a die of desired shape to a zone of reduced or lower pressure to form the foam. The zone of lower

pressure is at a pressure lower than that in which the foamable gel is maintained prior to extrusion through the die. The lower pressure may be superatmospheric or subatmospheric (vacuum), but is preferably at an atmospheric level.

5 The present foam comprises an alkenyl aromatic polymer material. Suitable alkenyl aromatic polymer materials include alkenyl aromatic homopolymers and copolymers of alkenyl aromatic compounds and copolymerizable ethylenically unsaturated comonomers. The alkenyl aromatic polymer material may further include minor proportions of non-alkenyl aromatic polymers. The alkenyl aromatic polymer material may be comprised solely of one or more alkenyl aromatic homopolymers, one or more alkenyl aromatic copolymers, a blend of  
10 one or more of each of alkenyl aromatic homopolymers and copolymers, or blends of any of the foregoing with a non-alkenyl aromatic polymer. Regardless of composition, the alkenyl aromatic polymer material comprises greater than 50 and preferably greater than 70 weight percent alkenyl aromatic monomeric units. Most preferably, the alkenyl aromatic polymer material is comprised entirely of alkenyl aromatic monomeric units.

15 Suitable alkenyl aromatic polymers include those derived from alkenyl aromatic compounds such as styrene, alphamethylstyrene, ethylstyrene, vinyl benzene, vinyl toluene, chlorostyrene, and bromostyrene. A preferred alkenyl aromatic polymer is polystyrene. Minor amounts of monoethylenically unsaturated compounds such as C<sub>2-6</sub> alkyl acids and esters, ionomeric derivatives, and C<sub>4-6</sub> dienes may be copolymerized with alkenyl aromatic  
20 compounds. Examples of copolymerizable compounds include acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, acrylonitrile, maleic anhydride, methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate and butadiene. Preferred foams comprise substantially (that is, greater than 95 percent) and most preferably entirely of polystyrene. Preferably, the alkenyl aromatic polymer foam is free of rubber  
25 content such as C<sub>4-6</sub> diene content and thermoset polymer content such as polyisocyanurate or polyurethane.

The present foam has the density of from 16 to 250 kilograms per cubic meter (kg/cm<sup>3</sup>) and most preferably from 25 to 100 kg/cm<sup>3</sup> according to ASTM D-1622-88.

30 The present foam has an average cell size of 70 micrometers or less, preferably 1 to 30 micrometers, and more preferably 1 to 20 micrometers, and most preferably from 1 micrometer to 10 micrometers according to ASTM D3576-77. The cell size or pore size (diameter) for the microcellular foams is determined according to ASTM D3576-77 except that measurement is taken from an enlarged photograph obtained by scanning electron microscopy instead of measurement taken directly from the foam.

35 The present foam may take any physical configuration known in the art such as sheet, plank, or rounds. The present foam is particularly suited to be formed into a plank, desirably one having a cross-sectional area of 30 square centimeters (cm<sup>2</sup>) or more and a minor dimension in cross-section (thickness) of 3/8 inch (0.95 cm) or more.

The present foam has an open cell content of 70 percent or more, preferably 90 percent or more, and most preferably 95 percent or more according to ASTM D2856-A.

5 The present foam may contain an infrared attenuating agent (IAA) to enhance its insulating performance. The IAA is composed of a different substance than the polymer substrate of the foam in which it is incorporated. The IAA may absorb or reflect infrared radiation or both. Useful IAA include particulate flakes of metals such as aluminum, silver, and gold and carbonaceous substances such as carbon black, activated carbon black and graphite. Useful carbon blacks include thermal black, furnace black, acetylene black, and channel black. Preferred IAA are thermal black and graphite. The IAA preferably comprises between 1.0 and 10 25 weight percent and preferably between 4.0 and 20 weight percent and most preferably 4.0 to 10 weight percent based upon the weight of the polymer material.

The use of certain IAA such as carbon black or graphite provides certain advantages and can actually enhance formation of the present foam. Carbon black and graphite provide additional nucleating action to make cell size smaller, cell walls thinner, and 15 create weak points in the cell walls. Thinner and weaker cell walls promote easier rupturing of the cell walls, and, thus, higher open cell content. Carbon black and graphite also increase gel viscosity, which allows a lower foaming temperature to be employed. The lower foaming temperature improves foam skin quality. The use of an IAA provides an additional advantage of inducing a greater proportional reduction in total foam thermal conductivity in 20 microcellular foams than in foams of larger average cell size, particularly those of cell size ranges 0.1 millimeter to 2.0 millimeters corresponding to conventional commercial closed-cell insulation foams.

The present foam is preferably substantially non-crosslinked, which means that the foam is substantially free of crosslinking. This is inclusive however, of the slight degree of 25 crosslinking which may occur naturally without the use of crosslinking agents or radiation. Substantially non-crosslinked foams contain no more than 5 percent gel per ASTM D-2765-84, method A.

Various additives may be incorporated in the present foam such as inorganic fillers, pigments, antioxidants, acid scavengers, ultraviolet absorbers, flame retardants, 30 processing aids, and extrusion aids.

An evacuated foam is a foam having within its cells a partial vacuum or near total vacuum of subatmospheric absolute pressure. An evacuated foam has preferably an absolute pressure of 10 torr or less, more preferably 1 torr or less, and most preferably 0.1 torr or less.

35 An unevacuated (non-evacuated) foam is a foam having within its cellular structure an atmospheric absolute pressure.

The present foam may be used to insulate a surface by applying to the surface an insulating panel fashioned from the present foam. Such panels are useful in any conventional insulating applications such as roofing, buildings, refrigerators.



The present foam is particularly useful as board stock in a hermetically-sealed vacuum panel. The panel may be formed as follows: a) the foam is placed inside a receptacle or enclosure such as a bag; b) the interior of the receptacle or enclosure and the foam are evacuated to a partial or near total vacuum (subatmospheric absolute pressure); and c) the  
5 receptacle or enclosure is sealed as to be air tight or hermetically sealed. The evacuated or vacuum panel is preferably evacuated to 10 torr or less, more preferably to 1 torr or less, and most preferably to 0.1 torr or less absolute pressure. The vacuum panel is useful in the insulating applications described above.

To further enhance the long-term performance of the vacuum panel, the  
10 evacuated interior of the panel may be provided with a "getter" material. The getter material absorbs gases and/or vapors which seep or permeate into the vacuum panel over time. Conventional getter materials include metal and metal alloys of barium, aluminum, magnesium, calcium, iron, nickel, and vanadium. Teachings to suitable getter materials include but are not limited to those set forth in U.S. Patent Nos. 5,191,980; 5,312,606; 5,312,607; and  
15 WO 93/25843.

Other types of useful getter materials include conventional dessicants, which are useful for adsorbing water vapor or moisture. Such materials are advantageously incorporated into the evacuated insulation panel in the form of a packet having a porous or permeable wrapper or receptacle containing the material therein. Useful materials include silica gel,  
20 activated alumina, aluminum-rich zeolites, calcium chloride, calcium oxide, and calcium sulfate. A preferred material is calcium oxide.

A useful evacuated panel employs as an enclosure formed of a laminate sheet of three or more layers. The outer layer comprises a scratch resistant material such as a polyester. The middle layer comprises a barrier material such as aluminum, polyvinyl chloride, and  
25 polyvinyl alcohol. The inner layer comprises a heat sealable material such as polyethylene or ethylene/acrylic acid copolymer.

The following are examples of the present invention, and are not to be construed as limiting. Unless otherwise indicated, all percentages, parts, or proportions are by weight based upon polymer weight.  
30

Extruded, open-cell, microcellular alkenyl aromatic polymer foams of the present invention were prepared as described below.

#### Example 1

Foams were prepared with two different extrusion systems, each comprising an extruder, a mixer, a cooler, and an extrusion die in series. The two systems operated at  
35 different extrusion rates, 10 pounds per hour (lb/hr) (4.5 kilograms/hour (kg/hr) and 220 lb/hr (100 kg/hr). They are referred to as the first and the second extrusion systems, respectively.

The foams of the first extrusion system were made with the following formulation: a blowing agent of 7.5 parts per hundred (pph) of HCFC-142b, 2.0 pph EtCl, and

1.4 pph CO<sub>2</sub>); optionally carbon black (Raven 430 of Cabot Corp.); 0.5 pph talc; a minor amount of calcium stearate; and a polystyrene resin of 200,000 weight average molecular weight according to size exclusion chromatography (SEC).

5 The foams of the second extrusion system were made with the following formulation: a blowing agent of 6.8 pph HFC-134a, 1.9 pph HFC-152a, and 0.6 pph CO<sub>2</sub>; carbon black (Thermal Black FT 239 of Huber Corp.); 0.4 pph talc; minor amount of calcium stearate; and polystyrene resin of 200,000 weight average molecular weight according to SEC.

10 Foams were made in both extrusion systems with various carbon black loadings and at various foaming temperatures. The R value for foams was measured at atmospheric pressure (760 torr) and in a vacuum (1 torr). R value was measured according to ASTM C-518-91 in an environmental pressure control system capable of maintaining its set point condition within  $\pm 0.01$  torr wherein the control system is employed in conjunction with a heat flow meter apparatus.

15 Microcellular foams of small average cell size and high open cell content were produced. Cell size, open cell content, density, and R value are set forth in Table 1. For microcellular foams made in both extrusion systems, increasing the level of carbon black increased R value.

#### Example 2

20 Foams of the present invention were prepared with the second extrusion system except as indicated below and in Table 2.

The foams were prepared with various blowing agents and mixtures thereof as specified in Table 2. The blowing agent loadings were pph based upon polymer weight. The foams were made with various carbon black loadings and at various foaming temperatures.

25 The R value for foams was measured at various pressures by the method set forth in Example 1.

Microcellular foams of small average cell size, high open cell content, and high R value were produced.

#### Example 3

30 Foams of the present invention were prepared with the second extrusion system except as indicated below and in Table 3.

The foams were prepared with various blowing agents and mixtures thereof as specified in Table 3. The blowing agent loadings were pph based upon polymer weight. The foams were made with various carbon black loadings and at various foaming temperatures.

35 The R value for foams was measured at various pressures by the method set forth in Example 1.

Microcellular foams of small average cell size, high open cell content, and high R value were produced.

**Example 4**

Foams of the present invention were prepared with the second extrusion system except as indicated below and in Table 4.

5 Microcellular foams of small average cell size and high open cell content were produced.

Due to the addition of carbon black, the cross-section of Run 42 could be made larger than that of Run 41. The carbon black increased gel viscosity, and allowed the die opening to be enlarged without losing die pressure and causing pre-foaming. The increase in die opening resulted in a foam of larger cross-section being produced. The larger cross-section  
10 affords improved skin quality and greater process versatility.

**Example 5**

Foams of the present invention were prepared with the second extrusion system except as indicated below and in Table 5.

15 The foams were prepared with various blowing agents and mixtures thereof as specified in Table 5. The blowing agent loadings were pph based upon polymer weight. The foams were made with various carbon black loadings and at various foaming temperatures.

The R value for foams was measured at various pressures by the method set forth in Example 1.

20 Microcellular foams of small average cell size, high open cell content, and high R value were produced.

25

30

35

Table 1  
Foams Prepared in Example 1

Run Number	Ext. Rate lb/hr (kg/hr)	Carbon Black (pph)	Foaming Temp. (°C)	Foam Density pcf (kg/m <sup>3</sup> )	Cell Size (mm)	Open Cell (percent)	R/inch 1 torr	R/inch 760 torr
1	10 (4.5)	10.0	155	1.82 (29.12)	0.04	99	7.41	---
2	10 (4.5)	15.0	145	1.94 (31.04)	0.02	99	13.7	---
3	220 (100)	0.0	133	2.75 (44)	0.02	94.6	9.09	3.92
4	220 (100)	7.0	132	3.31 (52.96)	0.011	92.7	15.38	4.37
5	220 (100)	10.0	132	4.15 (66.4)	0.006	95.7	16.13	4.52
6	220 (100)	15.0	132	4.08 (65.28)	0.01	94.3	17.86	4.55

Table 2  
Foams Prepared in Example 2

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Foam Density pcf (kg/m <sup>3</sup> )	Cell Size (mm)	Open Cell (percent)	R/inch 1 torr	R/inch 760 torr
7	9.0 HFC-134a / 3.0 EtCl	0.0	131	2.49 (39.84)	0.043	99.7	---	---
8	8.0 HFC-134a / 1.0 EtCl / 0.6 CO <sub>2</sub>	0.0	131	3.07 (49.12)	0.024	99.5	---	---
9	4.0 CO <sub>2</sub> / 0.5 EtOH	10.0	131	2.53 (40.48)	0.068	88.4	---	---
10	4.0 HFC-152a / 1.0 EtCl / 1.5 CO <sub>2</sub>	10.0	131	2.51 (40.16)	0.049	84.1	---	---
11	8.0 HFC-152a / 0.6 CO <sub>2</sub>	10.0	133	2.31 (36.96)	0.049	97.1	---	---
12	5.0 HFC-152a / 3.5 HFC-134a	10.0	133	2.32 (37.12)	0.038	95.5	---	---
13	6.8 HFC-134a / 1.9 HFC-152a / .27 Argon	10.0	131	4.39 (70.24)	0.005	94.3	16.39	---
14	6.8 HFC-134a / 2.4 HFC-152a / .19 N <sub>2</sub>	10.0	131	2.87 (45.92)	0.005	95.4	12.21	---

Table 2 (Continued)  
Foams Prepared in Example 2

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Foam Density pcf (kg/m <sup>3</sup> )	Cell Size (mm)	Open Cell (percent)	R/inch 1 torr	R/inch 760 torr
15	6.8 HFC-134a / 2.4 HFC-152a	10.0	131	5.13 (82.08)	0.005	93.3	14.29	---
16	6.8 HFC-134a / 2.4 HFC-152a / .34 Celogen AZ130 <sup>1</sup>	10.0	131	3.51 (56.16)	0.007	95.4	15.38	---
17	6.8 HFC-134a / 1.9 HFC-152a / 0.6 CO <sub>2</sub>	7.0	132	3.31 (52.96)	0.011	92.7	15.38	---
18	10.6 HFC-134a	6.9	127	3.48 (55.68)	0.025	98.0	---	---
19	8.5 HFC-134a / 0.9 HCFC-142b	6.9	125	4.35 (69.6)	0.008	98.0	---	---
20	7.0 HFC-143a / 0.9 HCFC-142b	6.9	126	4.08 (65.28)	0.007	---	---	---
21	5.5 HFC-143a / 2.4 HCFC-22	6.9	123	4.28 (68.48)	0.012	96.0	13.51	4.31
22	8.0 HCFC-22	6.9	130	3.15 (50.4)	0.065	97.0	---	---
23	8.4 HFC-134a / 0.8 HCFC-22	10.0	126	3.89 (62.24)	0.009	97.0	13.51	4.46

<sup>1</sup> Celogen AZ130 is a chemical blowing agent of Uniroyal Corp.

Table 3  
Foams Prepared in Example 3

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Cell Size (mm)	Open Cell (percent)	R/inch	Vacuum Pressure (torr)
24	8.0 HFC-134a/2.0 EtCl	0.0	131	0.041	95.5	12.5	0.0
25	8.0 HFC-134a/2.0 EtCl	0.0	131	0.041	95.5	8.62	1.0
26	8.0 HFC-134a/2.0 EtCl	0.0	131	0.041	95.5	6.58	5.0
27	8.0 HFC-134a/2.0 EtCl	0.0	131	0.041	95.5	5.71	10.0
28	8.0 HFC-134a/2.0 EtCl	10	129	0.048	96	18.18	0.0
29	8.0 HFC-134a/2.0 EtCl	10	129	0.048	96	11.49	1.0
30	8.0 HFC-134a/2.0 EtCl	10	129	0.048	96	7.25	5.0
31	8.0 HFC-134a/2.0 EtCl	10	129	0.048	96	6.02	10.0
32	8.6 HFC-134a/2.4 HFC-152a	10	123	0.005	98	18.0	0.0
33	8.6 HFC-134a/2.4 HFC-152a	10	123	0.005	98	12.4	1.0
34	8.6 HFC-134a/2.4 HFC-152a	10	123	0.005	98	9.5	5.0

Table 3 (Continued)  
Foams Prepared in Example 3

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Cell Size (mm)	Open Cell (percent)	R / inch	Vacuum Pressure (torr)
35	8.6 HFC-134a / 2.4 HFC-152a	10	123	0.005	98	7.0	10.0
36	7.5 HFC-134a / 2.0 HFC-152a	6.9	127	0.006	97	20.8	0.0
37	7.5 HFC-134a / 2.0 HFC-152a	6.9	127	0.006	97	18.87	1.0
38	7.5 HFC-134a / 2.0 HFC-152a	6.9	127	0.006	97	9.26	5.0
39	7.5 HFC-134a / 2.0 HFC-152a	6.9	127	0.006	97	5.09	10.0



Table 4  
Foams Prepared in Example 4

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Foam Density pcf (kg/m <sup>3</sup> )	Cell Size (mm)	Open Cell (percent)	Board Dimen. inch x inch (cm x cm) Ver. x Hor. <sup>1</sup>
40	8.0 HFC-134a / 1.0 EtCl / 0.6 CO <sub>2</sub>	0.0	131	3.07 (49.12)	0.030	99.5	3/8 x 2 1/2 (0.95 x 6.35)
41	8.0 HFC-134a / 1.0 EtCl / 0.6 CO <sub>2</sub>	10.0	131	2.60 (41.6)	0.040	98.6	5/8 x 3 1/2 (1.59 x 8.89)

<sup>1</sup> Ver. x Hor. - vertical direction and horizontal direction in cross-section

Table 5  
Foams Prepared in Example 5

Run Number	Blowing Agent	Carbon Black (pph)	Foaming Temp. (°C)	Foam Density pcf (kg/m <sup>3</sup> )	Cell Size (mm)	Open Cell (percent)	R/inch 1 torr	R/inch (R/cm) 760 torr
42	7.1 HFC-134a	10 pph syn graph <sup>1</sup>	130	3.82 (61.12)	0.009	100	20.6	---
43	7.1 HFC-134a	5 pph syn graph 5 pph ther black <sup>2</sup>	130	3.68 (58.88)	0.008	99	20.0	---
44	7.1 HFC-134a	10 pph nat graph <sup>3</sup>	131	3.66 (58.56)	0.007	95	18.3	---
45	12.2 HFC-134a	10 pph furn black <sup>4</sup>	130	2.96 (47.36)	0.008	98	17.2	---

<sup>1</sup> syn graph - synthetic graphite LS2849 of Graphite Products.

<sup>2</sup> ther black - thermal black FT 239 of Huber Corp.

<sup>3</sup> nat graph - natural graphite GP601 of Graphite Products.

<sup>4</sup> furn black - furnace black Monarch 1400 of Cabot Corp.

While embodiments of the microcellular foam and the process for making of the present invention have been shown with regard to specific details, it will be appreciated that depending upon the manufacturing process and the manufacturer's desires, the present  
5 invention may be modified by various changes while still being fairly within the scope of the novel teachings and principles herein set forth.

10

15

20

25

30

35

1. An open-cell microcellular alkenyl aromatic polymer foam comprising an alkenyl aromatic polymer material comprising greater than 50 percent by weight of alkenyl aromatic monomeric units and having a density of 16 to 250 kilograms per cubic meter, the foam being characterized in that it is extruded, the foam having an open cell content of 70 percent or more, the foam having an average cell size of 70 micrometers or less.
2. The foam of Claim 1, wherein the foam has an open cell content of 90 percent or more.
3. The foam of Claim 1 or 2, wherein the foam has an open cell content of 95 percent or more.
4. The foam of any of the preceding claims, wherein the foam has an average cell size of 1 micrometer to 30 micrometers.
5. The foam of any of the preceding claims, wherein the foam has an average cell size of 1 micrometer to 20 micrometers.
6. The foam of any of the preceding claims, wherein the foam has an average cell size of 1 micrometer to 10 micrometers.
7. The foam of any of the preceding claims, wherein the foam has a density of 25 to 100 kilograms per cubic meter.
8. The foam of any of the preceding claims, wherein the foam is an evacuated foam having an absolute pressure within its open cells of 10 torr or less.
9. The foam of any of the preceding claims, wherein the foam is an evacuated foam having an absolute pressure within its open cells of 1 torr or less.
10. The foam of any of the preceding claims, wherein the foam is an evacuated foam having an absolute pressure within its open cells of 0.1 torr or less.
11. An evacuated foam insulation panel, the panel comprising a foam and a receptacle capable of enclosing the foam and being hermetically-sealed, the foam being situated within the receptacle, the interior of the receptacle and the foam being evacuated to a subatmospheric pressure, the panel being characterized in that the foam is any of Claims 9-11.
12. A process for making an extruded, open-cell microcellular alkenyl aromatic polymer foam having an open cell content of 70 percent or more, comprising:
  - a) heating an alkenyl aromatic polymer material comprising more than 50 percent by weight alkenyl aromatic monomeric units to form a melt polymer material;
  - b) incorporating into the melt polymer material at an elevated pressure to form a foamable gel a blowing agent agent;
  - c) cooling the foamable gel to a desirable foaming temperature; and
  - d) extruding the foamable gel through a die into a region of lower pressure to form the foam, the process being characterized in that a nucleating agent additive is incorporated into the melt polymer material at from 0.1 to 5 parts by weight per hundred parts polymer material, 50 mole percent or more of a blowing agent selected from the group

consisting of 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, chlorodifluoroethane, carbon dioxide, and mixtures of the foregoing based upon the total number of moles of blowing agent, the blowing agent being present at 0.06 to 0.17 gram-moles per kilogram of polymer material, the foamable gel being cooled to a temperature

5 sufficient to form a foam having 70 percent or more open cell content.

13. The process of Claim 12, wherein the foamable gel is cooled to a temperature of 118°C to 160°C.

14. The process of Claim 12, wherein the foamable gel is cooled to a temperature of 125°C to 135°C.

10

15. The process of any of Claims 12-14, wherein the blowing agent is present at 0.08 to 0.12 gram-moles per kilogram of polymer material.

16. The process of any of Claims 12-15, wherein the blowing agent is 70 mole percent or more of a blowing agent selected from the group consisting of 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, chlorodifluoroethane, carbon dioxide, and

15 mixtures of the foregoing based upon the total number of moles of blowing agent.

17. The process of any of Claims 12-16, wherein the foamable gel is cooled to a temperature sufficient to form a foam having 90 percent or more open cell content, the foam having an average cell size of 1 to 30 micrometers.

18. The process of any of Claims 12-16, wherein the foamable gel is cooled to a

20 temperature sufficient to form a foam having 95 percent or more open cell content, the foam having an average cell size of 1 to 20 micrometers.

25

30

35

# INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/US 96/04009

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J9/14 C08J9/12 //C08L25:04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER, vol. 26, no. 11, 11 October 1985, pages 2047-2054, XP000575518 AUBERT & CLOUGH: "Low-density, microcellular polystyrene foams. " see page 2047	1-5,7
A	Paragraph : "Introduction" see page 2052 - page 2053 Paragraph : "Experimental" --- -/--	12-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

\* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* "&" document member of the same patent family

Date of the actual completion of the international search

8 July 1996

Date of mailing of the international search report

29.07.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Oudot, R

# INTERNATIONAL SEARCH REPORT

Intr. Application No  
PCT/US 96/04009

C.(Continuation) D. CUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>LANGMUIR : THE ACS JOURNAL OF SURFACES &amp; COLLOIDS, vol. 4, no. 1, January 1988 - February 1988, pages 44-49, XP002007743 JOEL M. WILLIAMS: "toroidal microstructures from water in oil emulsions" see page 44, line 1-5 see page 46, right-hand column, line 1-10</p>	1,4-7
A	<p>--- EP,A,0 265 356 (PECHINEY ALUMINIUM) 27 April 1988 see page 3, line 14-22 see page 3, line 42-46 see page 4; table 1 see claims 1-3</p>	1
A	<p>--- US,A,4 041 115 (JENKINS FRANCIS EDWARD ET AL) 9 August 1977 see claims -----</p>	12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/04009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-0265356	27-04-88	FR-A-	2605646	29-04-88
		AU-B-	591354	30-11-89
		AU-B-	8007287	28-04-88
		CA-A-	1332109	27-09-94
		IE-B-	60593	10-08-94
		JP-C-	1751568	08-04-93
		JP-B-	4038453	24-06-92
		JP-A-	63123439	27-05-88
		SU-A-	1637665	23-03-91
		US-A-	5424050	13-06-95
-----				
US-A-4041115	09-08-77	NONE		
-----				